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Azaphthalocyanines substituted with one aminogroup-influence of aliphatic substituents on intramolecular charge transfer.

At the beginning of my thesis I was working on synthesis of 1,2,6,7,11,12,16,17-octakis-[(4-dimethylamino)benzylidenamino] porphyrazine from *N,N*-bis[(4-dimethylamino)benzylidenamino]fumaronitrile and *N,N*-bis[(4-dimethylamino)benzylidenamino]maleonitrile. Cyclotetramerization was performed with magnesium butoxide, zinc acetate in quinoline or in *N,N*-dimethylformamide. Unfortunately, no product was obtained. As an alternative aim, I started to deal with synthesis of unsymmetrical azaphthalocyanines substituted with one amino group. The amino group is a donor in intramolecular charge transfer. This process competes with fluorescence and singlet oxygen formation and may lead to compounds useful as dark quenchers of fluorescence in hybridization probes.

I prepared a precursors, substituted pyrazine-2,3-dicarbonitriles, containing primary amino group, diethylamino- or butylamino- group. Prepared precursors were cyclotetramerized by method of statistical condensation. Cyclotetramerization was carried out in the presence of anhydrous magnesium butoxide. This method leads to six different congeners. The resulting magnesium complexes could not be separated due to extensive tailing on TLC. Magnesium was removed from the molecule by means of a strong acid (*p*-toluenesulfonic acid) and metal-free azaphthalocyanines were isolated. Subsequently, the central metal was complexed into the center of the molecule using zinc acetate or magnesium acetate.